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APPLICATION NO.	FILING DATE	. FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/735,370	12/12/2003	John Frederick Ackerman	130013/11921 (21635-0116)	1818
31450 7590 02/06/2007 MCNEES WALLACE & NURICK LLC 100 PINE STREET			EXAMINER BAREFORD, KATHERINE A	
11Alddoboko, 1A 1/100-1100			1762	
SHORTENED STATUTOR	Y PERIOD OF RESPONSE	MAIL DATE	DELIVERY MODE	
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# Please find below and/or attached an Office communication concerning this application or proceeding.

If NO period for reply is specified above, the maximum statutory period will apply and will expire 6 MONTHS from the mailing date of this communication.



	Application No.	Applicant(s)				
	10/735,370	ACKERMAN ET AL.				
Office Action Summary	Examiner	Art Unit				
	Katherine A. Bareford	1762				
The MAILING DATE of this communication app Period for Reply	ears on the cover sheet with the c	orrespondence address				
A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.  - Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.  - If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.  - Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).						
Status						
1) Responsive to communication(s) filed on 13 De	ecember 2006.					
2a)⊠ This action is <b>FINAL</b> . 2b)☐ This	action is non-final.					
3) Since this application is in condition for allowance except for formal matters, prosecution as to the merits is						
closed in accordance with the practice under E	x parte Quayle, 1935 C.D. 11, 45	33 O.G. 213.				
Disposition of Claims	•					
4) Claim(s) 1-21 is/are pending in the application.						
4a) Of the above claim(s) is/are withdraw	vn from consideration.	,				
5) Claim(s) is/are allowed.						
6)⊠ Claim(s) <u>1-7,9-11 and 13-21</u> is/are rejected.	6)⊠ Claim(s) <u>1-7,9-11 and 13-21</u> is/are rejected.					
· · · · · · · · · · · · · · · · · · ·	7) Claim(s) is/are objected to.					
8) Claim(s) are subject to restriction and/or Claims 8 and 12 are canceled	election requirement.	•				
Application Papers						
9) The specification is objected to by the Examiner.						
10) The drawing(s) filed on is/are: a) acce	10) The drawing(s) filed on is/are: a) accepted or b) objected to by the Examiner.					
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).						
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).						
11)☐ The oath or declaration is objected to by the Ex	aminer. Note the attached Office	Action or form PTO-152.				
Priority under 35 U.S.C. § 119						
<ul> <li>12) Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).</li> <li>a) All b) Some * c) None of:</li> <li>1. Certified copies of the priority documents have been received.</li> <li>2. Certified copies of the priority documents have been received in Application No.</li> <li>3. Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).</li> <li>* See the attached detailed Office action for a list of the certified copies not received.</li> </ul>						
Attachment(s)  1) Notice of References Cited (PTO-892)  2) Notice of Draftsperson's Patent Drawing Review (PTO-948)  3) Information Disclosure Statement(s) (PTO/SB/08)  Paper No(s)/Mail Date	4)  Interview Summary Paper No(s)/Mail Da 5)  Notice of Informal P 6)  Other:	(PTO-413) te				

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#### **DETAILED ACTION**

The amendment of December 13, 2006 has been received and entered.
 With the amendment, claims 1-7, 9-11 and 13-21 are pending, including new claims 19-21.

## Claim Rejections - 35 USC § 112

- 2. The following is a quotation of the first paragraph of 35 U.S.C. 112:
  - The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.
- 3. Claims 13-21 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

Independent claim 13 has been amended December 13, 2006 to provide forming a primary ceramic coating "wherein the primary ceramic coating has an excess of oxygen vacancies therein." Applicant has not provided where support for this amendment is located. A review of the application as originally filed provides only that when yttria is used with zirconia an excess of oxygen vacancies results (see paragraphs [0012] and [0030] of the specification). Thus, the use of a primary ceramic with an

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excess of oxygen vacancies is only supported as filed for when the coating is yttria stabilized zirconia, such as in claim 17, not for every possible ceramic. As a result, the claim contains new matter.

Independent claim 13 has also been amended December 13, 2006 to delete the requirement that cerium oxide with cerium in the +4 oxidation state is used and instead require that "cerium in an oxidation state that removes oxygen vacancies from the primary ceramic coating" is used. Applicant has not provided where support for this amendment is located. A review of the application as originally filed, provides only that cerium in the +4 oxidation state is always used (see paragraph [0029]), and while is described as removing oxygen vacancies (see paragraph [0030]), the claim as now worded allows for other oxidation states to be used (such as +3). As a result, the claim, contains new matter.

New independent claim 19 has been provided in the amendment of December 13, 2006 and requires forming a primary ceramic coating "wherein the primary ceramic coating has an excess of oxygen vacancies therein." Applicant has not provided where support for this amendment is located. A review of the application as originally filed provides only that when yttria is used with zirconia an excess of oxygen vacancies results (see paragraphs [0012] and [0030] of the specification). Thus, the use of a primary ceramic with an excess of oxygen vacancies is only supported as filed for when the coating is yttria stabilized zirconia, such as in claim  $\frac{2}{8}$ 0, not for every possible ceramic. As a result, the claim contains new matter.

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New independent claim 19 also requires providing that "a sintering-inhibitor region at a surface of the primary ceramic coating, wherein the sintering inhibiting region removes oxygen vacancies from the primary ceramic coating" is used. Applicant has not provided where support for this amendment is located. A review of the application as originally filed, provides only that cerium in the +4 oxidation state is always used (see paragraph [0029]), and while is described as removing oxygen vacancies (see paragraph [0030]), the claim as now worded allows for other oxidation states of cerium oxide to be used (such as +3) as well as entirely different materials from cerium oxide. As a result, the claim contains new matter.

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The other dependent claims do not cure all the defects of these claims from which they depend.

#### Claim Rejections - 35 USC § 103

- 4. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:
  - (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.
- 5. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were

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made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

6. Claims 13-21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Subramanian (US 6296945) in view of Stoffer et al (US 5932083).

Claims 13, 19: Subramanian teaches a method for preparing a protected article. Column 2, lines 20-40. The article is provided. Column 3, lines 50-68. A bond coat is deposited onto an exposed surface of the article. Column 4, lines 5-20 and figure 2. A thermal barrier coating is formed on an exposed surface of the bond coat. Column 4, lines 50-65 and figure 2. To form the thermal barrier coating, first a primary ceramic coating is applied to an exposed surface of the bond coat. Column 2, lines 25-45 (the "base" or "primary" ceramic is preferably yttria stabilized zirconia, for example). The surface of the primary coating comprises columnar grains with facing surfaces. See figures 2-3 and column 4, lines 55-60. This primary ceramic coating would have an excess of oxygen vacancies as the use of yttria stabilized zirconia is taught, which inherently has an excess of the oxygen vacancies. Column 2, lines 40-45. Then a sintering inhibiting material is applied to the surface of the primary ceramic coating. Column 2, lines 25-45, *column 5, lines 30-65 and figures 2-3 (the sheath material).* The sintering inhibiting region can comprise cerium oxide in a concentration greater than a general cerium oxide

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concentration in the primary ceramic coating. Column 2, line 65 through column 3, line 10 and column 5, lines 30-50 (cerium (Ce) can be provided as component C of the sheath material, thus providing  $Ce_zO_w$ , and furthermore, C is desirably not the A or B material of the primary ceramic (A = zirconia and B=yttria if yttria stabilized zirconia is used as the primary ceramic, for example)). The resulting applied material can be a stable oxide of  $C_zO_w$ , where C=Ce. Column 2, lines 35-40, column 4, lines 55-65 and column 5, lines 35-4. After the sintering inhibiting region is applied, there remain air filled gaps between the facing surfaces of the columnar grains. Figures 2-3 and column 5, lines 10-30.

Claim 14: the article is a nickel base superalloy article. *Column 3, lines 50-68*.

Claim 15: the article is in the form of a component for a gas turbine engine.

Column 3, lines 50-68.

Claim 16: the step of depositing the bond coat includes depositing an aluminum containing overlay bond coat. *Column 4, lines 5-20*.

Claim 17, 20: the primary ceramic coating can be yttria stabilized zirconia.

Column 2, lines 40-50.

Subramanian can be considered as teaching all the features of these claims except that the selected stable oxide of cerium is such that a +4 oxidation state of cerium is used and provides that the applied cerium oxide or sintering inhibitor region removes oxygen vacancies.

However, Stoffer indicates that cerium possesses two highly stable oxides,  $CeO_2$  or  $Ce_2O_3$ , in the oxidation states of 3 and 4. See column 2, lines 45-55.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Subramanian to select CeO<sub>2</sub> as the stable oxide of cerium to be used as suggested by Stoffer in order to provide a desirable sheath coating of cerium oxide, because Subramanian teaches to use a stable oxide of cerium as the coating material, and Stoffer teaches that a well known highly stable oxide of cerium is CeO<sub>2</sub>, which would have cerium in a +4 oxidation state (as oxygen has a +2 valence state). The use of CeO<sub>2</sub> would provide that the applied cerium oxide/sintering inhibitor region would inherently remove oxygen vacancies from the primary ceramic coating, because CeO<sub>2</sub> is a material that inherently provides such removal from yttria stabilized zirconia. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985).

7. Claims 1-5, 7, 9 and 13-21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Villiger et al (US 2001/003631) in view of Subramanian et al (US 6756082) (hereinafter Subramanian '082) and Liu, et al "Total Oxidation of Carbon Monoxide and Methane over Transition Metal-Fluorite Oxide Composite Catalysts" Article (hereinafter Liu Article).

Claims 1, 7, 9, 13, 19: Villiger teaches a method for preparing a protected article.

Paragraphs [0001]-[0003]. The article is provided. Paragraph [0014] (component 1). A

coating is formed on the component. Paragraph [0014] (coating 10). The coating can be a thermal barrier coating. Paragraph [0002] (with the function of increased temperature in use through thermal protective layers). To form the thermal barrier coating, first a primary ceramic coating is applied by thermal spraying, for example. Paragraph [0017] (the base coating 10 ceramic can be yttria and zirconia, for example). This primary ceramic coating would have an excess of oxygen vacancies as the use of yttria with zirconia is taught, which inherently has an excess of the oxygen vacancies. Paragraph [0017]. Then, a sealing medium 2, which is an aqueous or organic solution containing a salt of an oxidizable metal in solution is applied to the exposed surface 11 of the coating 10. Paragraphs [0014], [0019], [0025] and [0027]. The solution can contain a cerium oxide precursor such as cerium acetate (Ce (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>.3/2H<sub>2</sub>O), which is not "cerium oxide" with cerium in the +4 oxidation state". *Paragraph* [0027]. The solution infiltrates the coating 10 from the exposed surface 11. *Paragraph* [0019]. The applied solution is then heated to form the oxide of the metal salt by means of oxygen from the surroundings or from oxidizing agents in the solution. *Paragraph* [0020]. This would form cerium oxide in the case of cerium acetate. This would produce a sintering inhibitor region on the surface of the primary ceramic coating as cerium oxide is impregnated within the surface and on top of the ceramic coating 10. Furthermore, Villiger teaches that closed and large pores cannot be sealed off with the coating, thus indicating that although coating would be impregnated into the large pores, they would not be entirely closed

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off, leaving air filled gaps in the pores between facing surfaces of the pores. *Paragraph* [0032].

Claims 3, 15: the article is in the form of a component for a gas turbine engine.

Paragraph [0037] (the blade for the gas turbine).

Claim 5, 17: the primary ceramic coating can be yttria stabilized zirconia.

Paragraphs [0017] and [0034] (the combination of yttria and zirconia provides yttria stabilized zirconia).

Villiger teaches all the features of these claims except (1) that a bond coating is used under the primary ceramic coating (claims 1, 9, 13), (2) that the formed cerium oxide is in the +4 oxidation state and removes oxygen vacancies, (3) that the substrate is a nickel base superalloy (claims 2, 14), (4) the step of depositing the bond coat includes depositing an aluminum containing overlay bond coat (claims 4, 16), and (5) that the primary ceramic coating comprise columnar grains with facing surfaces on which the cerium oxide precursor is deposited to form sintering inhibiting regions (claims 1, 13) or is columnar (claim 9).

However, Subramanian '082 teaches that when applying thermal barrier layers to gas turbine components, it is well known to provide an aluminum containing overlay bond coating applied by plasma spraying before applying the ceramic thermal barrier coating by the thermal spray method of plasma spraying. *Column 5, lines 45-65 and column 1, lines 15-35*. Furthermore, the substrate of such gas turbine components is well known to be nickel based superalloys. *Column 5, lines 15-30*. As well, the ceramic

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thermal barrier coating is zirconia stabilized with about 8 wt% yttria, for example. Column 5, lines 60-65. Subramanian teaches that this ceramic thermal barrier coating applied by plasma spray or other methods is desirably in the form of a columnar microstructure. Column 4, lines 55-65 and figure 3. This provides a surface comprising columnar grains having facing surfaces. Figure 3. Moreover, a sintering inhibiting material is deposited onto the facing surfaces and partially filling the gaps but leaving air filled gaps between the facing surfaces. Figure 3 and column 6, lines 5-20.

Moreover, Liu Article teaches that cerium acetate when heated in air provides cerium oxide. *Page 305, section 2.1 ("Cerium acetate (99.9%, Aldrich), heated for 4 hours at 750°C in air, was used as the primary precursor of La-free cerium oxide."*). This cerium oxide is described as being CeO<sub>2</sub>. *Page 305, section 2.1 ("The physical mixture of ceria and copper oxide, CuO + CeO<sub>2</sub>, was prepared by blending the CuO and CeO<sub>2</sub> powders with water . . .", indicating that the formed cerium oxide from the cerium acetate is CeO<sub>2</sub>).* 

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger to use a gas turbine component with a nickel base superalloy substrate and to provide an aluminum containing overlay bond coating applied by plasma spraying before applying the thermally sprayed ceramic thermal barrier coating as suggested by Subramanian '082 with an expectation of providing a desirably protected thermal barrier coating made up of desirable components, because Villiger teaches partially sealing a thermal sprayed ceramic thermal barrier coating on a gas turbine component, and Subramanian '082 teaches that when providing a thermal

sprayed ceramic thermal barrier coating on a gas turbine component, it is well known to provide that the component is a nickel base superalloy and that a plasma sprayed aluminum containing overlay bond coating is provided on the component before applying the ceramic thermal barrier coating. Furthermore, it would further have been obvious to modify Villiger to provide that the ceramic thermal barrier coating is in the form of columnar grains with facing surfaces and that the coating acting as a sintering inhibitor material partially fills the pores or gaps between the columns as suggested by Subramanian '082 with an expectation of providing a desirably protective thermal barrier coating, because Villiger teaches that the thermal barrier coating material can be zirconia with yttria at, for example, 8% yttria and that the pores can be partially filled with a material that would be sintering inhibiting, and Subramanian '082 teaches that a desirable zirconia thermal barrier coating includes zirconia stabilized with 8% yttria and applied as columnar grains with facing surfaces and with an applied sintering inhibiting material that partially fills the pores of gaps between the columns. It would further have been obvious to modify the process of Villiger in view of Subramanian '082to select a precursor that provides CeO<sub>2</sub> as the formed oxide, which would provide that the cerium oxide precursor is such that the resulting cerium oxide is in the +4 valence state as suggested by Liu Article with an expectation of desirable protective sealing results, because Villiger teaches to oxidize cerium acetate and to oxidize using oxygen from the surroundings and Liu Article teaches that it is well known that when cerium acetate is oxidized to provide cerium oxide, CeO<sub>2</sub> is formed, which would have

cerium in a +4 oxidation state (as oxygen has a +2 valence state), and thus Villiger teaches that a cerium oxide precursor that results in cerium oxide with cerium in the +4 valence state can be desirably used. The use of CeO<sub>2</sub> would provide that the applied cerium oxide/sintering inhibitor region would inherently remove oxygen vacancies from the primary ceramic coating, because CeO<sub>2</sub> is a material that inherently provides such removal from yttria stabilized zirconia. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985).

8. Claims 6 and 11 are rejected under 35 U.S.C. 103(a) as being unpatentable over Villiger in view of Subramanian '082 and Liu Article as applied to claims 1-5, 7, 9 and 13-17 above, and further in view of Ueda et al (US 5697992).

Villiger in view of Subramanian '082 and Liu Article teaches all the features of these claims except using ammonium cerium sulfate as the precursor. Villiger does teach that salts of the oxidizable metal can be used as the precursors, and describes cerium nitrate and cerium acetate as possible precursors. *Paragraphs* [0027] and [0027].

Ueda teaches that cerium oxide can be provided by providing a precursor of the oxide in liquid, and that a well known cerium compound precursor for this purpose that converts to cerium oxide by calcining is ammonium cerium sulfate. *See column 4, lines 20-30.* The calcining provides heating to perform the conversion. *Column 4, lines* 

20-30 and 40-50. Heating methods include vacuum and non vacuum heating devices (which would provide heating in air). See column 4, lines 60-68. Ueda also teaches that cerium nitrates and cerium acetates are also known precursors for converting to metal oxides. Column 4, lines 20-30.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger in view of Subramanian '082and Liu Article to use ammonium cerium sulfate as a precursor for cerium oxide as suggested by Ueda with an expectation of desirable formation of cerium oxide because Villiger in view of Subramanian '082 and Liu Article teaches that salts of the oxidizable metal can be used as the precursors, and describes cerium nitrate and cerium acetate as possible precursors and Ueda teaches that cerium acetate, cerium nitrates and ammonium cerium sulfate would all be known acceptable precursors for making cerium oxide by heating.

9. Claim 10 is rejected under 35 U.S.C. 103(a) as being unpatentable over Villiger in view of Subramanian '082 and Liu Article as applied to claims 1-5, 7, 9 and 13-17 above, and further in view of Taylor et al (US 5520516).

Villiger in view of Subramanian '082 and Liu Article teaches all the features of this claim except using 7 percent zirconia by weight in the primary ceramic coating.

Taylor teaches that when forming a vertically cracked, or columnar, thermal barrier coating of zirconia on a gas turbine engine component by plasma spraying, it is

well known to use about 7 to 8 weight percent yttria stabilized zirconia. *Column 5, lines* 5-40 and column 1, lines 5-15.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger in view of Subramanian '082and Liu Article to use 7 weight percent zirconia as suggested by Taylor with an expectation of providing a desirable primary yttria stabilized zirconia coating because Villiger in view of Subramanian '082 and Liu Article teaches that the thermal barrier coating material can be zirconia with yttria, at for example 8% yttria (se Villiger and Subramanian '082), and Taylor teaches that desirable zirconia thermal barrier coating material includes about 7 to 8 wt% yttria.

10. Claims 1-5, 7, 9, 10 and 13-21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Villiger et al (US 2001/003631) in view of Taylor et al (US 5520516) and Liu, et al "Total Oxidation of Carbon Monoxide and Methane over Transition Metal-Fluorite Oxide Composite Catalysts" Article (hereinafter Liu Article).

Claims 1, 7, 9, 13, 19: Villiger teaches a method for preparing a protected article. Paragraphs [0001]-[0003]. The article is provided. Paragraph [0014] (component 1). A coating is formed on the component. Paragraph [0014] (coating 10). The coating can be a thermal barrier coating. Paragraph [0002] (with the function of increased temperature in use through thermal protective layers). To form the thermal barrier coating, first a primary ceramic coating is applied by thermal spraying, for example. Paragraph [0017] (the base

coating 10 ceramic can be yttria and zirconia, for example). This primary ceramic coating would have an excess of oxygen vacancies as the use of yttria with zirconia is taught, which inherently has an excess of the oxygen vacancies. Paragraph [0017]. Then, a sealing medium 2, which is an aqueous or organic solution containing a salt of an oxidizable metal in solution is applied to the exposed surface 11 of the coating 10. Paragraphs [0014], [0019], [0025] and [0027]. The solution can contain a cerium oxide precursor such as cerium acetate (Ce  $(C_2H_3O_2)_3.3/2H_2O$ ), which is not "cerium oxide" with cerium in the +4 oxidation state". Paragraph [0027]. The solution infiltrates the coating 10 from the exposed surface 11. Paragraph [0019]. The applied solution is then heated to form the oxide of the metal salt by means of oxygen from the surroundings or from oxidizing agents in the solution. Paragraph [0020]. This would form cerium oxide in the case of cerium acetate. This would produce a sintering inhibitor region on the surface of the primary ceramic coating as cerium oxide is impregnated within the surface and on top of the ceramic coating 10. Furthermore, Villiger teaches that closed and large pores cannot be sealed off with the coating, thus indicating that although coating would be impregnated into the large pores, they would not be entirely closed off, leaving air filled gaps in the pores between facing surfaces of the pores. Paragraph [0032].

Claims 3, 15: the article is in the form of a component for a gas turbine engine.

Paragraph [0037] (the blade for the gas turbine).

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Claim 5, 17: the primary ceramic coating can be yttria stabilized zirconia.

Paragraphs [0017] and [0034] (the combination of yttria and zirconia provides yttria stabilized zirconia).

Villiger teaches all the features of these claims except (1) that a bond coating is used under the primary ceramic coating (claims 1, 9, 13), (2) that the formed cerium oxide is in the +4 oxidation state and removes oxygen vacancies, (3) that the substrate is a nickel base superalloy (claims 2, 14), (4) the step of depositing the bond coat includes depositing an aluminum containing overlay bond coat (claims 4, 16), (5) that the yttria stabilized zirconia is 7 percent yttria by weight and (6) that the primary ceramic coating comprise columnar grains with facing surfaces on which the cerium oxide precursor is deposited to form sintering inhibiting regions (claims 1, 13) or is columnar (claim 9).

However, Taylor teaches that when forming a vertically cracked, or columnar, thermal barrier coating of zirconia on a gas turbine engine component by plasma spraying, it is well known to use about 7 to 8 weight percent yttria stabilized zirconia. *Column 5, lines 5-40 and column 1, lines 5-15.* Furthermore, Taylor teaches that it is well known to provide an aluminum containing overlayer bond coating by plasma sprayng under the zirconia coating. *Column 5, lines 25-40.* Furthermore, the substrate can be a superalloy, and can be a nickel base alloy. *Column 5, lines 25-40.* 

Moreover, Liu Article teaches that cerium acetate when heated in air provides cerium oxide. *Page 305, section 2.1 ("Cerium acetate (99.9%, Aldrich), heated for 4 hours at 750°C in air, was used as the primary precursor of La-free cerium oxide."*). This cerium oxide

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is described as being CeO<sub>2</sub>. Page 305, section 2.1 ("The physical mixture of ceria and copper oxide, CuO + CeO<sub>2</sub>, was prepared by blending the CuO and CeO<sub>2</sub> powders with water . . .", indicating that the formed cerium oxide from the cerium acetate is CeO<sub>2</sub>).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger to use a gas turbine component with a nickel base superalloy substrate and to provide an aluminum containing overlay bond coating applied by plasma spraying before applying the thermally sprayed ceramic thermal barrier coating as suggested by Taylor with an expectation of providing a desirably protected thermal barrier coating made up of desirable components, because Villiger teaches partially sealing a thermal sprayed ceramic thermal barrier coating on a gas turbine component, and Taylor teaches that when providing a thermal sprayed ceramic thermal barrier coating on a gas turbine component, it is well known to provide that the component is a nickel base and superalloy and that a plasma sprayed aluminum containing overlay bond coating is provided on the component before applying the ceramic thermal barrier coating. It would further have been obvious to to modify Villiger to use 7 weight percent zirconia as suggested by Taylor with an expectation of providing a desirable primary yttria stabilized zirconia coating because Villiger teaches that the thermal barrier coating material can be zirconia with yttria, at for example 8% yttria, and Taylor teaches that desirable zirconia thermal barrier coating material includes about 7 to 8 wt% yttria. Furthermore, it would further have been obvious to modify Villiger to provide that the ceramic thermal barrier coating is in the form of

columnar grains with facing surfaces and that the coating acting as a sintering inhibitor material partially fills the pores or gaps between the columns as suggested by Taylor with an expectation of providing a desirably protective thermal barrier coating, because Villiger teaches that the thermal barrier coating material can be zirconia with yttria at, for example, 8% yttria and that the pores can be partially filled with a material that would be sintering inhibiting, and Taylor teaches that a desirable zirconia thermal barrier coating includes zirconia stabilized with 7-8% yttria and applied as columnar grains (vertical macrocracks) which would have facing surfaces forming pores. It would further have been obvious to modify the process of Villiger in view of Taylor to select a precursor that provides CeO<sub>2</sub> as the formed oxide, which would provide that the cerium oxide precursor is such that the resulting cerium oxide is in the +4 valence state as suggested by Liu Article with an expectation of desirable protective sealing results, because Villiger teaches to oxidize cerium acetate and to oxidize using oxygen from the surroundings and Liu Article teaches that it is well known that when cerium acetate is oxidized to provide cerium oxide, CeO2 is formed, which would have cerium in a +4 oxidation state (as oxygen has a +2 valence state), and thus Villiger teaches that a cerium oxide precursor that results in cerium oxide with cerium in the +4 valence state can be desirably used. The use of CeO<sub>2</sub> would provide that the applied cerium oxide/sintering inhibitor region would inherently remove oxygen vacancies from the primary ceramic coating, because CeO<sub>2</sub> is a material that inherently provides such removal from yttria stabilized zirconia. The fact that applicant has recognized another

advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See Ex parte Obiaya, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985).

Claims 6 and 11 are rejected under 35 U.S.C. 103(a) as being unpatentable over 11. Villiger in view of Taylor and Liu Article as applied to claims 1-5, 7, 9, 10 and 13-17 above, and further in view of Ueda et al (US 5697992).

Villiger in view of Taylor and Liu Article teaches all the features of these claims except using ammonium cerium sulfate as the precursor. Villiger does teach that salts of the oxidizable metal can be used as the precursors, and describes cerium nitrate and cerium acetate as possible precursors. *Paragraphs* [0027] and [0027].

Ueda teaches that cerium oxide can be provided by providing a precursor of the oxide in liquid, and that a well known cerium compound precursor for this purpose that converts to cerium oxide by calcining is ammonium cerium sulfate. See column 4, lines 20-30. The calcining provides heating to perform the conversion. Column 4, lines 20-30 and 40-50. Heating methods include vacuum and non vacuum heating devices (which would provide heating in air). See column 4, lines 60-68. Ueda also teaches that cerium nitrates and cerium acetates are also known precursors for converting to metal oxides. Column 4, lines 20-30.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger in view of Taylor and Liu Article to use

ammonium cerium sulfate as a precursor for cerium oxide as suggested by Ueda with an expectation of desirable formation of cerium oxide because Villiger in view of Taylor and Liu Article teaches that salts of the oxidizable metal can be used as the precursors, and describes cerium nitrate and cerium acetate as possible precursors and Ueda teaches that cerium acetate, cerium nitrates and ammonium cerium sulfate would all be known acceptable precursors for making cerium oxide by heating.

12. Claims 19-21 are rejected under 35 U.S.C. 103(a) as being unpatentable over Villiger et al (US 2001/003631) in view of Vine et al (US 4861618) and Liu, et al "Total Oxidation of Carbon Monoxide and Methane over Transition Metal-Fluorite Oxide Composite Catalysts" Article (hereinafter Liu Article).

Claim 19: Villiger teaches a method for preparing a protected article. Paragraphs [0001]-[0003]. The article is provided. Paragraph [0014] (component 1). A coating is formed on the component. Paragraph [0014] (coating 10). The coating can be a thermal barrier coating. Paragraph [0002] (with the function of increased temperature in use through thermal protective layers). To form the thermal barrier coating, first a primary ceramic coating is applied by thermal spraying, for example. Paragraph [0017] (the base coating 10 ceramic can be yttria and zirconia, for example). This primary ceramic coating would have an excess of oxygen vacancies as the use of yttria with zirconia is taught, which inherently has an excess of the oxygen vacancies. Paragraph [0017]. Then, a sealing medium 2, which is an aqueous or organic solution containing a salt of an oxidizable

metal in solution is applied to the exposed surface 11 of the coating 10. *Paragraphs* [0014], [0019], [0025] and [0027]. The solution can contain a cerium oxide precursor such as cerium acetate (Ce (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>.3/2H<sub>2</sub>O), which is not "cerium oxide with cerium in the +4 oxidation state". *Paragraph* [0027]. The solution infiltrates the coating 10 from the exposed surface 11. *Paragraph* [0019]. The applied solution is then heated to form the oxide of the metal salt by means of oxygen from the surroundings or from oxidizing agents in the solution. *Paragraph* [0020]. This would form cerium oxide in the case of cerium acetate. This would produce a sintering inhibitor region on the surface of the primary ceramic coating as cerium oxide is impregnated within the surface and on top of the ceramic coating 10.

Claim 20: the primary ceramic coating can be yttria stabilized zirconia.

Paragraphs [0017] and [0034] (the combination of yttria and zirconia provides yttria stabilized zirconia).

Villiger teaches all the features of these claims except (1) that a bond coating is used under the primary ceramic coating (claims19), (2) that the formed cerium oxide is in the +4 oxidation state and removes oxygen vacancies.

However, Vine teaches that when applying thermal barrier layers to gas turbine components, it is well known to provide an aluminum containing overlay bond coating applied by plasma spraying before applying the ceramic thermal barrier coating by the thermal spray method of plasma spraying. *Column 2, lines 25-45 and column 1, lines 5-30*. Vine teaches that the bond coat helps provide beneficial performance of the thermal

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barrier coating. *Column 4, lines 55-65*. Furthermore, the substrate of such gas turbine components is well known to be nickel based superalloys. *Column 1, lines 20-35*. As well, the ceramic thermal barrier coating is zirconia stabilized with 6-8 wt% yttria, desirably 7 % yttria. *Column 6, lines 5-10 and 25-35 and column 2, lines 35-45*.

Moreover, Liu Article teaches that cerium acetate when heated in air provides cerium oxide. *Page 305, section 2.1 ("Cerium acetate (99.9%, Aldrich), heated for 4 hours at 750°C in air, was used as the primary precursor of La-free cerium oxide."*). This cerium oxide is described as being CeO<sub>2</sub>. *Page 305, section 2.1 ("The physical mixture of ceria and copper oxide, CuO + CeO<sub>2</sub>, was prepared by blending the CuO and CeO<sub>2</sub> powders with water . . .", indicating that the formed cerium oxide from the cerium acetate is CeO<sub>2</sub>).* 

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify Villiger to provide a bond coating applied by plasma spraying before applying the thermally sprayed ceramic thermal barrier coating as suggested by Vine with an expectation of providing a desirably protected thermal barrier coating made up of desirable components, because Villiger teaches sealing a thermal sprayed ceramic thermal barrier coating on a gas turbine component, and Vine teaches that when providing a thermal sprayed ceramic thermal barrier coating on a gas turbine component, it is well known to provide that a plasma sprayed bond coating is provided on the component before applying the ceramic thermal barrier coating and helps coating performance. It would further have been obvious to modify the process of Villiger in view of Vine to select a precursor that provides CeO<sub>2</sub> as the formed oxide,

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which would provide that the cerium oxide precursor is such that the resulting cerium oxide is in the +4 valence state as suggested by Liu Article with an expectation of desirable protective sealing results, because Villiger teaches to oxidize cerium acetate and to oxidize using oxygen from the surroundings and Liu Article teaches that it is well known that when cerium acetate is oxidized to provide cerium oxide, CeO<sub>2</sub> is formed, which would have cerium in a +4 oxidation state (as oxygen has a +2 valence state), and thus Villiger teaches that a cerium oxide precursor that results in cerium oxide with cerium in the +4 valence state can be desirably used. The use of CeO<sub>2</sub> would provide that the applied cerium oxide/sintering inhibitor region would inherently remove oxygen vacancies from the primary ceramic coating, because CeO<sub>2</sub> is a material that inherently provides such removal from yttria stabilized zirconia. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985).

13. Bowker et al (US 6231998) teaches that yttria stabilized zirconia inherently has high oxygen vacancy concentration. Column 3, lines 23-30. Rigney et al (US 6586115) also teaches the known oxygen vacancy concentration in yttria stabilized zirconia and the known use of CeO<sub>2</sub> to affect this. Column 3, lines 10-45.

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## Response to Arguments

14. Applicant's arguments filed December 13, 2006 have been fully considered but they are not persuasive as to the rejection of claims 13-21 using Subramanian view of Stoffer.

As to the argument that neither reference provides that the primary ceramic has an excess of oxygen vacancies, it is the Examiner's position that it is known by those skilled in the art that yttria stabilized zirconia, taught by Subramanian, inherently has an excess of oxygen vacancies. Furthermore, the use of the CeO<sub>2</sub> suggested by the combination of the references will inherently remove oxygen vacancies. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985). The combination of references provides the application of CeO<sub>2</sub> onto a primary ceramic of yttria stabilized zirconia as a sintering inhibiting material, which are the precise process steps indicated by applicant as providing removal of oxygen vacancies.

As to the rejection of new claims 19-21 using Villiger in view of Vine and Liu, applicant has provided no separate arguments as to claims 19-21. The Examiner notes that these clams do not require a columnar primary ceramic coating, or air filled gaps. As to the oxygen vacancies and the material that removes oxygen vacancies, it is the

Examiner's position that it is known by those skilled in the art that yttria stabilized zirconia, taught by Villiger and Vine, inherently has an excess of oxygen vacancies. Furthermore, the use of the CeO<sub>2</sub> suggested by the combination of the references will inherently remove oxygen vacancies. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985). The combination of references provides the application of CeO<sub>2</sub> onto a primary ceramic of yttria stabilized zirconia as a sintering inhibiting material, which are the precise process steps indicated by applicant as providing removal of oxygen vacancies.

15. Applicant's arguments with respect to claims 1-7, 9-11 and 13-21 have been considered but are most in view of the new ground(s) of rejection.

As to applicant's arguments as to the use of Villiger in view of Vine and Liu Article, the Examiner has provided new rejections using Villiger in view of Subramanian '082 and Liu Article, and also using Villiger in view of Taylor and Liu Article based on the amendments to claims 1, 9 and 13 as to providing columnar primary ceramic coatings. As to the excess of oxygen vacancies in claims 13 and 19, and the cerium in an oxidiation state to remove oxygen vacancies (claim 13) and sintering inhibitor region to remove oxygen vacancies (claim 19), it is the Examiner's position that it is known by those skilled in the art that yttria stabilized zirconia, taught by Villiger,

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Subramania '082 and Taylor, inherently has an excess of oxygen vacancies.

Furthermore, the use of the CeO<sub>2</sub> suggested by the combination of the references will inherently remove oxygen vacancies. The fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985). The combination of references provides the application of CeO<sub>2</sub> onto a primary ceramic of yttria stabilized zirconia as a sintering inhibiting material, which are the precise process steps indicated by applicant as providing removal of oxygen vacancies.

As to the argument as to claims 6 and 11 that Ueda is non-analogous art, in response to applicant's argument that Ueda is nonanalogous art, it has been held that a prior art reference must either be in the field of applicant's endeavor or, if not, then be reasonably pertinent to the particular problem with which the applicant was concerned, in order to be relied upon as a basis for rejection of the claimed invention. See *In re Oetiker*, 977 F.2d 1443, 24 USPQ2d 1443 (Fed. Cir. 1992). In this case, Ueda is reasonably pertinent to the problem of applicant of providing CeO<sub>2</sub> from a precursor. As taught by Villiger, salts of the oxidizable metal are desirably used as precursors and includes cerium nitrate and cerium acetate as possible precursors, Ueda is used as a teaching reference to show well known cerium compounds that can be used as precursors to forming cerium oxide include cerium nitrate, cerium acetate and ammonium cerium sulfate.

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#### Conclusion

16. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

17. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Katherine A. Bareford whose telephone number is (571) 272-1413. The examiner can normally be reached on M-F(6:00-3:30) with the First Friday Off.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Timothy Meeks can be reached on (571) 272-1423. The fax phone numbers for the organization where this application or proceeding is assigned are (571) 273-8300 for regular communications and for After Final communications.

Other inquiries can be directed to the Tech Center 1700 telephone number at (571) 272-1700.

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Furthermore, information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <a href="http://pair-direct.uspto.gov">http://pair-direct.uspto.gov</a>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

KATHERINE BAREFORD PRIMARY EXAMINER